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Organometallic Nonlinear Optical (NLO) Polymers. 2. Synthesis of Main-Chain Organometallic Polymers and a Structural Study of Ferrocene NLO-phores

by

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A detailed structural analysis of several ferrocene based NLO-phores were examined by X-ray diffraction. Structures were reported for $\{\eta^5\text{-}C_5H_5\}\{\eta^5\text{-}C_5H_4CH=C(CN)(R)\}Fe$ [where **1a**, R = CO_2Et; **1b**, R= CN; **1c**, R = 4-pyridyl; **1d**, R = 4-bromophenyl]. Through selective functionalization of the cyclopentadienyl rings of ferrocene new monomers, namely $\{\eta^5\text{-}C_5H_4CH_2O(CH_2)_nOH\}\{\eta^5\text{-}C_5H_4CH=C(CN)CO_2Et\}Fe$ (**5**) and $\{\eta^5\text{-}C_5H_4CH_2O\text{-}(CH_2)_nO_2CCH_2CN\}\{\eta^5\text{-}C_5H_4CHO\}Fe$ [**6**, n= 6; **8**, n= 1], were prepared in the study. The transesterification polymerization resulted in formation of an intractable polymeric material of unknown structure. The homopolymerization of **6** by the Knoevenagel technique afforded the desired polymer **9a**, albeit in low molecular weight $\{M_n = \sim 6700\}$.

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Abstract. A detailed structural analysis of several ferrocene based NLO-phores were examined by X-ray diffraction. Structures were reported for $\{\eta^5\text{-}C_5H_5\}\{\eta^5\text{-}C_5H_4CH=C(CN)(R)\}Fe$ [where **1a**, R = CO_2Et; **1b**, R= CN; **1c**, R = 4-pyridyl; **1d**, R = 4-bromophenyl]. The study illustrated that electron-withdrawing groups favor and control planarity of the π-system. Through selective functionalization of the cyclopentadienyl rings of ferrocene new monomers, namely $\{\eta^5\text{-}C_5H_4CH_2O(CH_2)_nOH\}\{\eta^5\text{-}C_5H_4CH=C(CN)CO_2Et\}Fe$ (**5**) and $\{\eta^5\text{-}C_5H_4CH_2O(CH_2)_nO_2CCH_2CN\}\{\eta^5\text{-}C_5H_4CHO\}Fe$ [**6**, n= 6; **8**, n= 1], were prepared in the study. Monomer **5** was suitable for Lewis acid catalyzed transesterification-polymerization using $Ti(OC_4H_9)_4$ and **6** and **8** were appropriate for a Knoevenagel polycondensation. The transesterification polymerization resulted in formation of an intractable polymeric material of unknown structure. The homopolymerization of **6** by the Knoevenagel technique afforded the desired polymer **9a**, albeit in low molecular weight $\{M_n = \sim 6800\}$. The polymer was characterized by GPC and spectroscopic data. A major by-product in the polymerization was the macrocyclic lactone, **10a**, produced from an intramolecular Knoevenagel condensation. The lactone structure was confirmed by single-crystal X-ray diffraction.
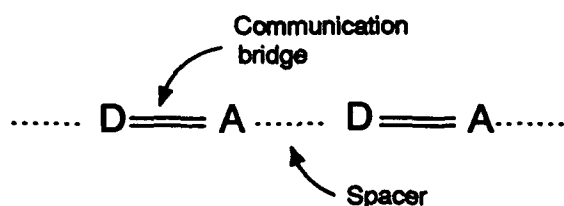
[End of Abstract]

Introduction

The discovery of ferrocene over four decades ago marked the beginning of organometallic chemistry.[1] The ferrocene unit has proved itself to be a versatile building block with excellent thermal and photochemical stability.[2] Polymeric materials which contain organometallic moieties have become a well developed and mature subdisipline of polymer chemistry.[3] The ferrocene unit has been incorporated into polymers as a pendant group[4] and also as part of the polymer backbone.[5]

M = Mo(NO)(L)Cl
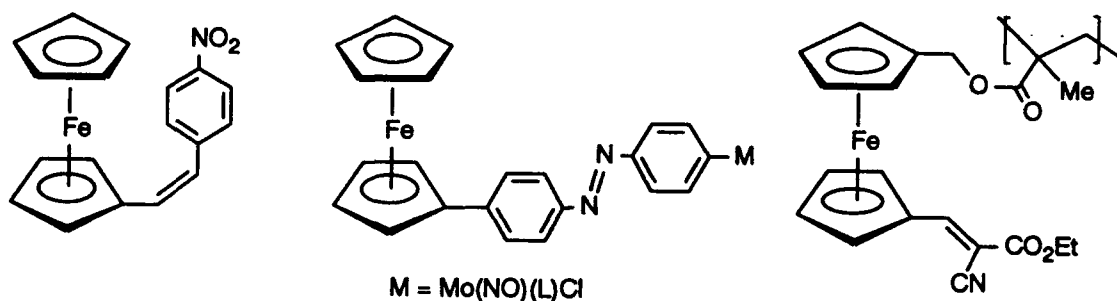
A very recent use of ferrocene complexes has appeared in the area of nonlinear optical (NLO) materials.[6] Based on both theory[7] and experimental data,[8] ferrocene compounds possess large hyperpolarizability values (i.e. β). These data combined with excellent thermal and photochemical stability make ferrocene systems a top organometallic candidate for use in NLO materials.[9] Our research program has recently demonstrated that a ferrocene complex bound to poly(methyl methacrylate) copolymer can be successfully aligned and exhibit second harmonic generation (SHG).[10]

2

Communication
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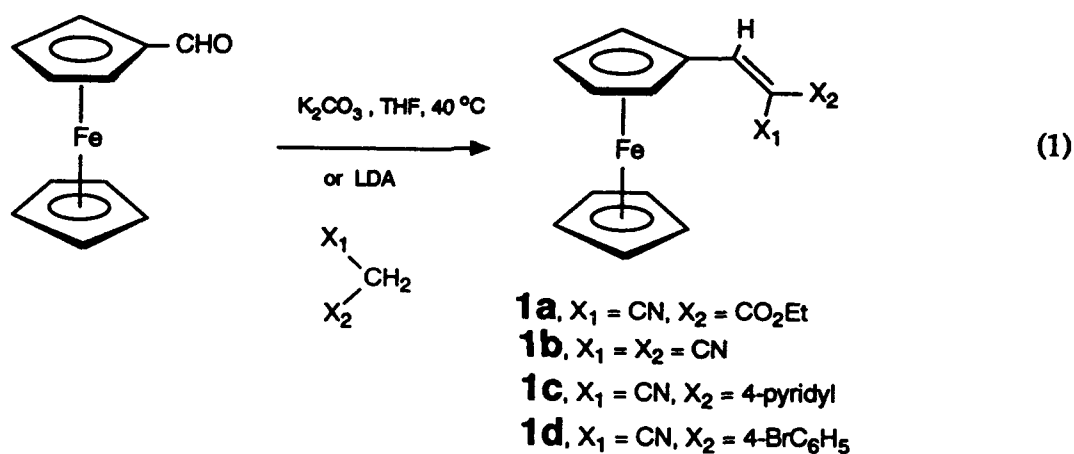········ D ══ A ········ D ══ A ········

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Linear Main-Chain NLO Polymer

The design and synthesis of new NLO materials for SHG applications can be accomplished through a variety of strategies.[11]   One such scheme involves the incorporation of the NLO active unit in the polymer backbone.[12, 13]   Organometallic coordination polymers containing transition metal acetylide linkages have been exploited in $\chi^{(3)}$ nonlinear optical applications.[14]   In addition, Thompson and coworkers have reported the synthesis of AB dipolar coordination polymers based on pyridine coordination to chromium, manganese, and iron complexes.[15] Theory indicates that alignment of polymer chains containing a series of repeating units will have a significant enhancement in $\chi^{(2)}$ nonlinear optical properties.

In the first segment of this paper we present a molecular structural analysis of ferrocene NLO-phores. We then describe several novel monomer syntheses and finally their utilization in the synthesis of main-chain organometallic NLO-phore based polymers.

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Results & Discussion

Crystallographic Study of Ferrocene NLO-phores   Treatment of ferrocenecarboxaldehyde with active methylene compounds results in high yields of the condensation product 1 (eq 1).[16] For the preparation of 1c and 1d we employed lithium diisopropylamide in place of K_2CO_3. The reactions proceed in nearly quantitative yield with no apparent side reactions.

$$\text{(eq 1)} \qquad K_2CO_3, \text{ THF, } 40\ ^\circ C \quad \text{or LDA}$$

$$\begin{aligned}
&\textbf{1a}, X_1 = CN, X_2 = CO_2Et\\
&\textbf{1b}, X_1 = X_2 = CN\\
&\textbf{1c}, X_1 = CN, X_2 = \text{4-pyridyl}\\
&\textbf{1d}, X_1 = CN, X_2 = \text{4-BrC}_6\text{H}_5
\end{aligned}$$

(1)

Four ferrocene NLO-phores have been characterized by single-crystal molecular structure determinations. Drawings of the molecular-structures are presented in Figure 1 and a summary of crystallographic data is presented in Table 1. Several structural features are worth noting. In all the systems we have prepared to date the cyano group is found in a Z-relationship to the ferrocenyl moiety. The coplanarity of the system appears related to the electronic nature of the substituents on the vinyl group. Notably, the *p*-bromophenyl group in 1d is rotated considerably out plane from the alkene π-system; whereas, it can be seen that the 4-pyridyl in 1c is nearly coplanar with the π-

4

system. Although we believe this to be an electronic effect, this does not rule out the possibility that we are observing a packing effect.

****
Insert Figure 1 & Table 1
**

Monomer Synthesis. Through chemistry developed in our laboratory we can prepare complex **2** starting from readily available materials.[17] Compound **2** is smoothly O-alkylated and then treated with *n*-BuLi and DMF to afford complex **3** (Scheme 1). Removal of the dimethyl-*tert*-butylsilyl protecting group using

Scheme 1
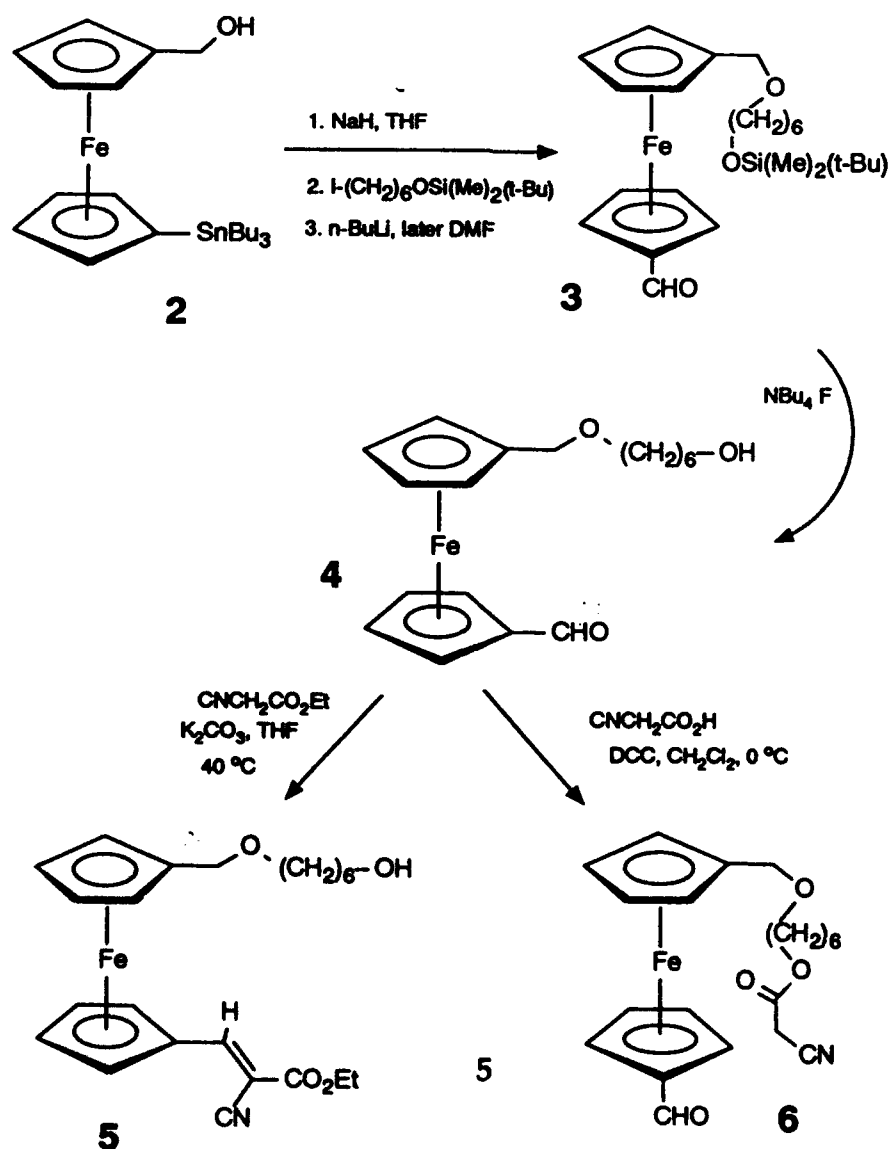
tetrabutylammonium flouride affords complex **4** which serves as a pivital intermediate in our synthetic strategy. Treatment of **4** with ethyl cyanoacetate in the presence of potassium carbonate affords monomer **5**. Coupling of **4** with cyanoacetic acid using dicyclohexylcarbodiimide (DCC) affords the AB monomer **6**. Monomer **6** is found to be very base sensitive and rapidly undergoes an intramolecular Knoevenagel condensation which makes purification procedures extremely difficult.

Starting once again at a *bis*(functionalized) ferrocene complex[17] previously synthesized in our laboratory we carried out the synthesis of monomers **7** and **8** (eq 2). The latter monomer is sensitive to purification techniques and in fact polymerizes/cyclizes on standing. This is not surprising considering the ease of enolization for the cyanoacetate group. Since these are AB monomers we can tolerate impurities so long as they do not obstruct the polymerization reaction.


(2)
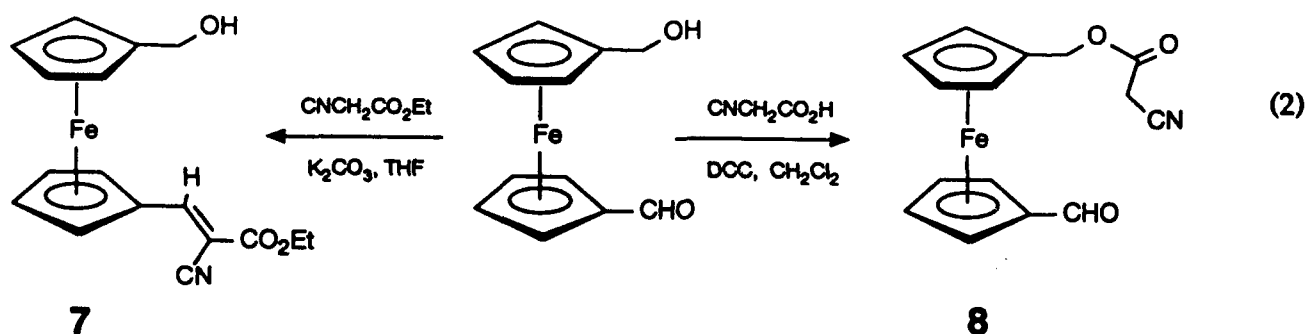
Polymer Synthesis & Characterization. We first attempted to polymerize monomer **5** by treatment with $Ti(OC_4H_9)_4$ and heating the mixture to 150 °C under a

nitrogen atmosphere (Scheme 2). The product of the polymerization reaction is an intractable purple solid. Carrying out the polymerization at 200 °C as a neat melt produces a similar intractable purple solid. In this latter case we identified 1,6-hexanediol as a volatile by-product of the "polymerization" reaction. We have seen similar results when polymerizing monomer 7.[17] The intractable purple solid exhibits spectroscopic (IR and UV-Vis) and analytical data close to that expected for the desired polyester.

Scheme 2
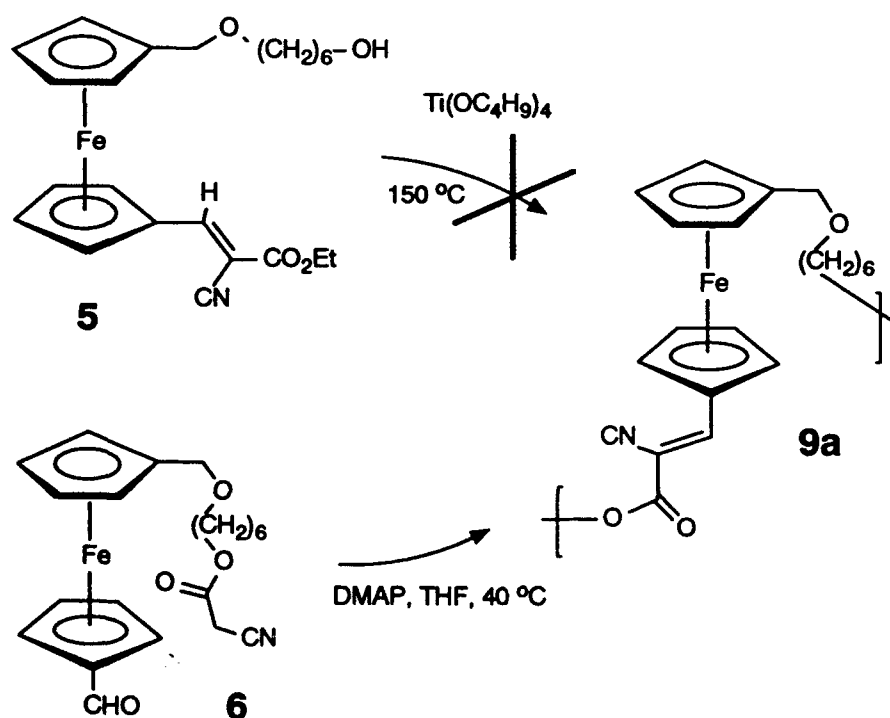
Treatment of **6** with *N,N*-dimethylaminopyridine (DMAP) at 40 °C produces polymer **9a**. Polymer **9a** is found to be of low molecular weight (M_n = ~4,500) and possesses both aldehyde and cyanoacetate end-groups. Polymer **9a** is soluble in organic solvents and displays spectroscopic data consistent with the ferrocenyl NLO-phore (*i.e.* β-ferrocenyl-α-cyanoacrylate). Further treatment of polymer **9a** (M_n = 4,500) with new monomer produced polymer of higher molecular wieght (M_n = ~6,800). We believe a limiting factor in the polymerization of **6** is an intramolecular Koevenagel condensation which competes with polymer formation (eq 3).[18] The macrocyclic lactone **10a** is isolated from the polymerization reaction by selective crystallization. A single-crystal X-ray diffraction study has been completed and drawing of the structure is shown in Figure 2.

6, Z = O(CH₂)₆O
7, Z = O

10a, Z = O(CH₂)₆O
10b, Z = O

(3)

Dilute Conditions

K₂CO₃ or alumina
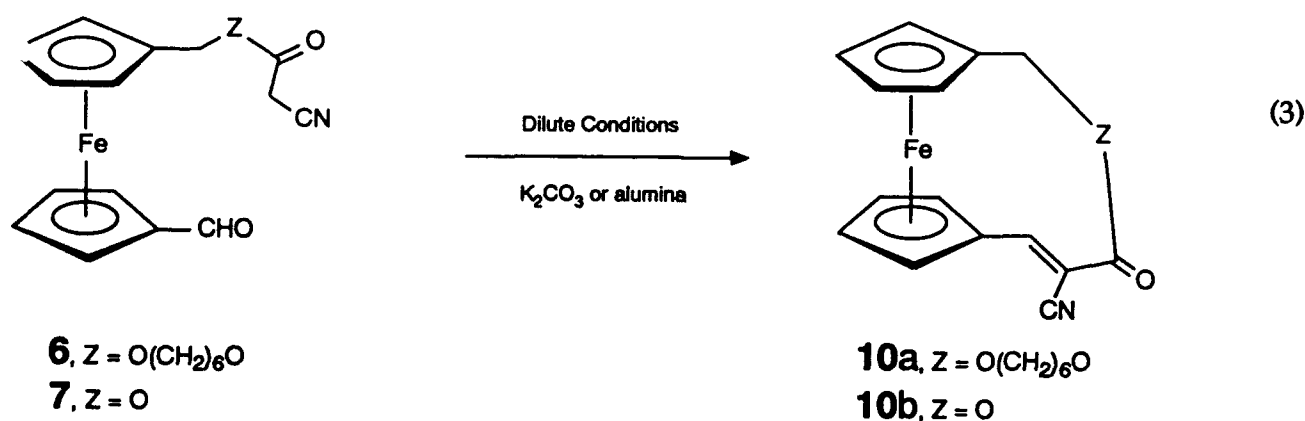
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Insert Figure 2 here
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8

Polycondensation of monomer 8 using base catalysis produces the macrocyclic lactone 10b as the major product along with the oligomer 9b (M_n = 1,400). Attempts to circumvent lactone formation by an increase in reactant concentrations are unsuccessful.

Concluding Remarks

Structural studies performed in this work illustrate that coplanarity in the ferrocenyl-NLO-phores is controlled by electron-withdrawing groups on the vinyl group. This is best seen by comparison of structures 1c and 1d. Synthetic efforts have produced new monomers and a new class of ferrocene based NLO-phore homopolymers. Employing the Koevenagel polycondensation reaction affords homopolymers of modest molecular weight. These polymers are tractable materials unlike those obtained through transesterfication or neat melt polymerization techniques. Work is continuing on the design of new monomers which are less likely to undergo an intramolecular Koevenagel condensation.

Experimental Details

General. All manipulations of compounds and solvents were carried out using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents. Spectroscopic measurements utilized the following instrumentation: ^{1}H NMR, Varian XL 300; ^{13}C NMR, JEOL 270 (at 67.80 MHz). NMR chemical shifts are reported as δ assigning CDCl$_3$ resonance at 7.25 ppm in ^{1}H and assigning the CDCl$_3$ resonance at 77.00 ppm in ^{13}C spectra. The ferrocenecarboxaldehyde, ethyl cyanoacetate, 4-bromophenylacetonitrile, Bu$_4$NF (1 M in THF), and malononitrile were all purchased from Aldrich Chemical and used as received. The 4-pyridylacetonitrile hydrochloride was suspended in ether, neutralized with NaHCO$_3$, and then dried under vacuum. GPC data was collected on a Varian 5000 HPLC employing a PL size-exclusion mixed gel column (300 x 7.5 mm, 5μ particle size). Molecular weight data is referenced relative to polystyrene standards (polystyrene standards ranged from 1,300 to 3,000,000). Polymer analysis were performed using a Perkin Elmer TGA 7 and DSC 7 system. Elemental analyses were performed at Atlantic Microlab Inc, Norcross, Georgia.

(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$CH=C(CN)C$_5$H$_4$N)Fe (1c). A LDA (8.5 mmol) solution is generated in THF at -78 °C. This solution was cannula transferred into a Schlenk flask containing 4-pyridylacetonitrile (1.0 g, 8.5 mmol) and THF (10 mL). This was allowed to react for 1 h at -78 °C. This solution was then cannula transferred into a Schlenk flask containing a THF (10 mL) solution of ferrocenecarboxaldehyde (1.82 g, 8.5 mmol) at -78 °C. The resulting solution was allowed to warm to room temperature. The mixture was

diluted with ether (100 mL) and the organic layer washed with water (2 x 100 mL), brine and then dried over K_2CO_3. The solvent was removed under reduced pressure and the crude product subjected to column chromatography (3 x 10 cm) on alumina. Gradient elution starting with methylene chloride and finishing with $MeOH/CH_2Cl_2$ (1/99, v/v), afforded pure 1c as purple crystals (2.19 g, 82%, m.p. 142-3 °C). ^1H NMR ($CDCl_3$) δ 8.61 (m, 2 H, py), 7.61 (s, 1 H, C$\underline{H}$=C), 7.46 (m, 2 H, py), 4.99 (t, 2 H, J= 2 Hz, Cp), 4.61 (t, 2 H, J= 2 Hz, Cp), 4.23 (s, 5 H, Cp); ^{13}C NMR ($CDCl_3$) δ 150.4 (py), 146.9 ($\underline{C}H$=), 141.9 (py), 119.0 (py), 118.0 ($\underline{C}$≡N), 103.6 (=$\underline{C}$(CN)), 76.2 (*ipso*-Cp), 72.6 (Cp CH), 70.7 (Cp CH), 70.0 (C_5H_5); IR (CH_2Cl_2) $v_{C≡N}$ 2215, $v_{C=C}$ 1592 cm^{-1}; UV-Vis (CH_2Cl_2) 510 (ε = 1.83 x 10^3) nm. Anal. Calcd for $C_{18}H_{14}FeN_2$: C, 68.81; H, 4.49; N, 8.92%. Found: C, 68.67; H, 4.73; N, 8.70%.

{η^5-C$_5$H$_5$}{η^5-C$_5$H$_4$CH=C(CN)C$_6$H$_4$Br}Fe (1d). A THF LDA (2.35 mmol) solution was cannula transferred into a Schlenk flask containing a chilled (-78 °C) THF (10 mL) solution of 4-bromophenylacetonitrile (0.28 g, 2.4 mmol). The mixture was allowed to react at -78 °C for 1 h and then cannula transferred into a Schlenk flask containing a THF (10 mL) solution of ferrocenecarboxaldehyde (0.50 g, 2.4 mmol) chilled to -78 °C. The cooling bath was removed and mixture allowed to warm to ambient temperature. The mixture was diluted with ether (100 mL) and the organic layer washed with water (2 x 100 mL), brine (100 mL), and dried over K_2CO_3. The solvent was removed under reduced pressure and the crude product subjected to column chromatography (2 x 15 cm) on alumina. Elution with EtOAc/hexanes (1/20, v/v) gave a dark red band which was collected and the solvents removed to afford pure 1d as deep red crystals (0.79 g,

84%, mp 140-141 °C). ^{1}H NMR (CDCl$_3$) δ 7.49 (m, 4 H, Ar), 7.37 (s, 1 H, C$\underline{H}$=), 4.95 (t, 2 H, J= 2 Hz, Cp), 4.54 (t, 2 H, J= 2 Hz, Cp), 4.23 (s, 5 H, Cp); ^{13}C NMR (CDCl$_3$) δ 143.7 ($\underline{C}$H=), 133.6 (Ar C), 132.0 (Ar CH), 126.5 (Ar CH), 122.0 (Ar C), 118.6 ($\underline{C}$≡N), 105.3 (=$\underline{C}$(CN)), 77.0 (*ipso*-Cp), 71.7 (Cp CH), 70.1 (Cp CH), 69.8 (C$_5$H$_5$); IR (CH$_2$Cl$_2$) $v_{C\equiv N}$ 2213, $v_{C=C}$ 1600 cm^{-1}; UV-Vis (CH$_2$Cl$_2$) 500 (ε = 2.62 x 10^3) nm. Anal. Calcd for C$_{19}$H$_{14}$BrFeN: C, 58.20; H, 3.60%. Found: C, 58.10; H, 3.60%.

X-ray diffraction study of Complexes 1. Crystals of **1** were grow through slow diffusion of pentane into a chloroform solution of the appropriate complex (**1a-d**). Crystals were mounted on glass fibers and secured by epoxy cement. Unit cells were determined through centering on at least 15 reflections with 2θ greater than 15°. Intensity data were collected on a Siemens P4 diffractometer. The structure solution (direct methods) and refinement was accomplished using the SHELXTL PLUS package of programs. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined in an idealized geometry (riding model at 0.95 Å) with set isotropic thermal parameters. Table 1 supplies a summary of pertinent crystal data, collection parameters, and details of the refinement for each complex. Atomic positions for all atoms and thermal parameters for non-hydrogen atoms have been filed with the Cambridge Structural data base.

{η^5-C$_5$H$_4$CH$_2$O(CH$_2$)$_6$OSi(Me)$_2$(t-Bu)}{η^5-C$_5$H$_4$CHO}Fe (3). A chilled (-78 °C) THF solution of **3** (1.54 g, 2.1 mmol) was treated with *n*-BuLi (0.85 mL, 2.1 mmol) and allowed to react for 30 min. DMF (0.33 mL, 4.2 mmol) was added and the cooling bath removed.

After the mixture reached ambient temperature it was diluted with ether (100 mL) and the organic layer washed with water (2 x 100 mL), brine (100 mL), and finally dried over K$_2$CO$_3$. The solvent was removed under reduced pressure and the crude product subject to column chromatography (3 x 10 cm) on alumina. Gradient elution starting with (EtOAc/hexanes, 1/20, v/v) ending with (EtOAc/hexanes, 1/4, v/v). The first orange band was collected and the solvents removed under reduced pressure to afford **4** as and orange oil (0.76 g, 79% yield). ^{1}H NMR (CDCl$_3$) δ 9.85 (s, 1 H, C_HO), 4.74 (t, J= 2 Hz, 2 H, Cp), 4.56 (t, J= 2 Hz, 2 H, Cp), 4.31 (t, J= 2 Hz, 2 H, Cp), 4.23 (t, J= 2 Hz, 2 H, Cp), 4.19 (s, 2 H, C_H$_2$O), 3.58 (t, J= 6.5 Hz, 2 H, C_H$_2$O), 3.41 (t, J= 6.6 Hz, 2 H, SiOC_H$_2$), 1.56 (m, 4 H, C_H$_2$'s), 1.32 (m, 4 H, C_H$_2$'s), 0.88 (s, 9 H, t-Bu), 0.03 (s, 6 H, C_H$_3$); ^{13}C NMR (CDCl$_3$) δ 193.0 (_CHO), 86.1 (*ipso*-Cp), 79.6 (*ipso*-Cp), 73.4 (Cp CH), 70.3 (Cp_CH$_2$O), 70.1 (Cp CH), 69.9 (Cp CH), 69.5 (Cp CH), 67.7 (O_CH$_2$), 63.0 (O_CH$_2$), 32.6, 29.5 (CH$_2$'s), 25.8 (C(_CH$_3$)$_3$), 25.7, 18.1 (_CH$_2$'s), 15.1 (_C(CH$_3$)$_3$), -5.40 (Si_CH$_3$); IR (CH$_2$Cl$_2$) $v_{C=O}$ = 1682 cm^{-1}; UV-Vis (CH$_2$Cl$_2$) 460 (ε= 5.2 x 10^4) nm. Anal. Cacld for C$_{24}$H$_{38}$FeOSi: C, 62.87; H, 8.35%. Found: C, 62.48; H, 8.20%.

{η^5-C$_5$H$_4$CH$_2$O(CH$_2$)$_6$OH{η^5-C$_5$H$_4$CHO}Fe (4). A THF solution of **4** (1.07 g, 2.33 mmol) was treated with Bu$_4$N$^+$F$^-$ (4.66 mL, 4.66 mmol) and allowed to react with stirring at room temperature for 6 h. The mixture was diluted with ether (100 mL) and the organic layer washed with water (2 x 100 mL), brine (100 mL), and then dried over K$_2$CO$_3$. The solvent was removed under reduced pressure and the crude product subjected to column chromatography (3 x 10 cm) on alumina. Gradient elution starting with CH$_2$Cl$_2$ and finishing with MeOH/CH$_2$Cl$_2$ (1/20, v/v) yields an orange oil (0.40 g,

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50%). ^{1}H NMR (CDCl$_3$) δ 9.89 (s, 1 H, C$\underline{H}$O), 4.72 (t, J= 2.0 Hz, 2 H, Cp), 4.55 (t, J= 2.0 Hz, 2 H, Cp), 4.29 (t, J= 2.0 Hz, 2 H, Cp), 4.21 (t, J= 2.0 Hz, 2 H, Cp), 4.11 (s, 2 H, CpC$\underline{H}_2$O), 3.60 (q, J= 6.2 Hz, 2 H, OC$\underline{H}_2$), 3.40 (t, J= 6.5 Hz, 2 H, C$\underline{H}_2$OH), 1.64 (s, 1 H, O$\underline{H}$), 1.54 (m, 4 H, C$\underline{H}_2$), 1.34 (m, 4 H, C$\underline{H}_2$); ^{13}C NMR (CDCl$_3$) δ 193.3 ($\underline{C}$HO), 85.9 (*ipso*-Cp), 79.4 (*ipso*-Cp), 73.5 (Cp CH), 70.5 (Cp$\underline{C}$H$_2$O), 70.1 (Cp CH), 69.8 (Cp CH), 69.5 (Cp CH), 67.6 (O$\underline{C}$H$_2$), 62.2 ($\underline{C}$H$_2$OH), 32.4, 29.3, 25.7, 25.3 ($\underline{C}$H$_2$'s); IR (CH$_2$Cl$_2$) $\nu_{C=O}$ 1681 cm^{-1}; UV-Vis (CH$_2$Cl$_2$) 460 (ε= 2.45 x 10^3) nm. Anal. Calcd for C$_{18}$H$_{24}$O$_3$: C, 62.81; H, 7.03%. Found: C, 62.47; H, 7.05%.

{η^5-C$_5$H$_4$CH$_2$O(CH$_2$)$_6$OH}{η^5-C$_5$H$_4$CH=C(CN)CO$_2$Et}Fe (5).   A THF (5 mL) solution of 4 (0.14 g, 0.41 mmol) was treated with ethyl cyanoacetate (0.044 mL, 0.41 mmol) and an excess of K$_2$CO$_3$ (5-10 mol-equiv). This mixture was heated and maintained at 40 °C for 12 h. The resulting purple solution was filtered and the solvent removed under reduced pressure to afford a purple oil. The crude mixture was subjected to column chromatography (2 x 5 cm) on alumina. Elution with CH$_2$Cl$_2$ and collection of the purple band follwed by removal of the solvents afforded pure 4 as an oil (0.135 g, 75%). ^{1}H NMR (CDCl$_3$) δ 8.13 (s, 1 H, C$\underline{H}$O), 5.04 (t, 2 H, Cp), 4.68 (t, 2 H, Cp), 4.30 (q, J= 7.1 Hz, 2 H, C$\underline{H}_2$CH$_3$), 4.28 (t, J= 2 Hz, 2 H, Cp), 4.22 (t, J= 2 Hz, 2 H, Cp), 4.12 (s, 2 H, CpC$\underline{H}_2$O), 3.86 (m, 2 H, OC$\underline{H}_2$), 3.40 (t, J= 6.5 Hz, 2 H, C$\underline{H}_2$OH), 1.73 (br s, 1 H, O$\underline{H}$), 1.55 (m, 4 H, C$\underline{H}_2$), 1.36 (t, J= 7.1 Hz, 3 H, C$\underline{H}_3$); ^{13}C NMR (CDCl$_3$) δ 163.2 ($\underline{C}$O$_2$Et), 158.4 ($\underline{C}$H=), 116.7 ($\underline{C}$N), 97.3 (CH=$\underline{C}$(CN)), 86.8 (*ipso*-Cp), 74.5 (Cp CH), 72.2 (Cp CH), 71.1 (Cp CH), 70.6 (Cp CH), 70.4 (CpO$\underline{C}$H$_2$), 67.8 (O$\underline{C}$H$_2$CH$_3$), 62.7 ($\underline{C}$H$_2$O), 62.0 ($\underline{C}$H$_2$O), 32.6, 29.5, 25.8, 25.4 ($\underline{C}$H$_2$'s), 14.1 ($\underline{C}$H$_3$). Anal. Calcd for C$_{23}$H$_{29}$O$_4$N: C, 62.88; H, 6.65; N, 3.19%.

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Found: C, 62.79; H, 6.63; N, 3.19%.

{η⁵-C₅H₄CH₂O(CH₂)₆O₂CCH₂CN}{η⁵-C₅H₄CHO}Fe **(6)**. A chilled (0 °C) CH₂Cl₂ (2
mL) solution of **5** (0.25 g, 0.70 mmol) was treated with cyanoacetic acid (60 mg, 0.7
mmol) and DCC (0.2 g, 0.7 mmol). The mixture was allowed to react with stirring at 0
°C for 2 h. The mixture was filtered through celite to remove the dicyclohexylurea and
the solvent was removed under reduced pressure to afford crude **6** (0.23g, 73%). ¹H
NMR (CDCl₃) δ 9.91 (s, 1 H, C$\underline{H}$O), 4.75 (t, *J*= 2 Hz, 2 H, Cp), 4.57 (t, *J*= 2 Hz, 2 H, Cp),
4.31 (t, *J*= 2 Hz, 2 H, Cp), 4.24 (t, *J*= 2 Hz, 2 H, Cp), 4.19 (t, *J*= 6.6 Hz, 2 H, C$\underline{H}$₂O), 4.13 (s,
2 H, CpC$\underline{H}$₂O), 3.44 (s, 2 H, C$\underline{H}$₂CN), 3.41 (t, *J*= 6.5 Hz, 2 H, OC$\underline{H}$₂), 1.67 (m, 2 H, C$\underline{H}$₂),
1.56 (m, 2 H, C$\underline{H}$₂), 1.36 (m, 4 H, C$\underline{H}$₂); ¹³C NMR (CDCl₃) δ 193.8 ($\underline{C}$HO), 162.9 ($\underline{C}$O₂),
113.1 ($\underline{C}$N), 85.7 (*ipso*-Cp), 79.2 (*ipso*-Cp), 73.8 (Cp CH), 70.3 (Cp CH), 70.0 (Cp CH), 69.9
(Cp$\underline{C}$H₂O), 69.7 (Cp CH), 67.6 ($\underline{C}$H₂O₂C), 66.6 (O$\underline{C}$H₂), 33.1 , 29.1, 28.0, 25.4, 25.2, 24.5
($\underline{C}$H₂'s).

{η⁵-C₅H₄CH₂O₂CCH₂CN}{η⁵-C₅H₄CHO}Fe **(8)**. A chilled (0 °C) THF solution of {η⁵-
C₅H₄CH₂OH}{η⁵-C₅H₄CHO}Fe (0.72 g, 2.9 mmol) was treated with cyanoacetic acid (0.25
g, 2.9 mmol) and dicyclohexylcarbodiimide (0.61 g, 2.9 mmol). The mixture was allowed
to react with stirring at 0 °C for 2 h. The mixture was filtered through celite and the
solvent removed under reduced pressure to afford crude **8** (0.69 g, 75%). ¹H NMR
(CDCl₃) δ 9.94 (s, 1 H, C$\underline{H}$O), 4.93 (s, 2 H, CpC$\underline{H}$₂O), 4.80 (t, *J*= 2 Hz, 2 H, Cp), 4.62 (t, *J*=
2 Hz, 2 H, Cp), 4.38 (t, *J*= 2 Hz, 2 H, Cp), 4.31 (t, *J*= 2 Hz, 2 H, Cp), 3.46 (t, *J*= 7.4 Hz, 2
H, C$\underline{H}$₂O); ¹³C NMR (CDCl₃) δ 193.9 ($\underline{C}$HO), 163.4 ($\underline{C}$O₂), 113.9 ($\underline{C}$N), 82.3 (*ipso*-Cp), 80.1

(*ipso*-Cp), 74.2 (Cp CH), 71.0 (Cp CH), 70.8 (Cp CH), 70.6 (Cp CH), 64.2 ($\underline{C}H_2O$), 25.0 ($\underline{C}H_2CN$); IR (CH_2Cl_2) $\nu_{C=O}$ 1751 and 1682, $\nu_{C\equiv N}$ 2305 cm^{-1}.

Polymer 9a A Schlenk flask was charged with THF (3 mL), 6 (0.34 g, 0.83 mmol), and DMAP (0.10 g, 0.83 mmol). The mixture was heated to 40 °C and allowed to react for 16 h. The reaction mixture was decanted into pentane (100 mL) and the precipitated polymer collected (0.38 g, 43%). The polymer was contaminated with small amounts of lactone **10a**. GPC analysis of the polymer gave an average molecular weight of M_n= 4,560 with a polydispersity of ~ 1.6. GPC analysis of the polymer showed about 30% of was lactone. A THF solution containing the polmer/lactone mixture (0.03 g) and 6 (0.91 g, 2.21 mmol) was treated with DMAP (0.27 g, 2.21 mmol) in an attempt to increase the molecular weight. GPC analysis of this product showed a peak corresponding to an average molecular weight of M_n= 6,800 with a polydispersity of ~ 2.0. GPC analysis of the polymer showed about 30% was lactone. Spectroscopic data for the polymer: ^{1}H NMR (CDCl$_3$) δ 8.13 (s, 1 H, C$\underline{H}$O), 4.98 (t, *J*= 2 Hz, 2 H, Cp), 4.72 (t, *J*= 2 Hz, 2 H, Cp), 4.29 (t, *J*= 2 Hz, 2 H, *ipso*-Cp), 4.24 (m, 4 H, Cp and C$\underline{H}_2$O), 4.13 (s, 2 H, CpC$\underline{H}_2$O), 3.42 (m, 2 H, OC$\underline{H}_2$), 1.74 (m, 2 H, C$\underline{H}_2$), 1.59 (m, 2 H, C$\underline{H}_2$), 1.41 (m, 4 H, C$\underline{H}_2$); ^{13}C NMR (CDCl$_3$) δ 163.2 ($\underline{C}O_2$), 158.4 ($\underline{C}H=$), 116.8 ($\underline{C}N$), 86.8 (*ipso*-Cp), 77.3 (*ipso*-Cp), 74.6 (Cp CH), 72.2 (Cp CH), 71.2 (Cp CH), 70.8 (Cp CH), 70.4 (Cp$\underline{C}H_2O$), 68.0 ($\underline{C}H_2O$), 66.1 ($\underline{C}H_2O$), 29.5, 28.5, 25.7, 25.5 ($\underline{C}H_2$'s).

Polymer 9b. A THF solution containing 7 (0.96 g, 3.1 mmol) was treated with DMAP (0.38 g, 3.1 mmol) and allowed to react for 48 h. The resulting mixture was

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crashed out in pentane and the solid collected and dried. NMR spectra of the "mixture" showed that the primary products were isomeric lactone complexes. Subsequent GPC analysis gave a small peak $M_n = 1,400$ while the majority of the sample gave a molecular weight corresponding to lactone.

Lactone 10a. The lactone was obtained by selective crystallization by diffusing pentane (through the vapor phase) into a $CHCl_3$ solution of the polymer mixture. ^1H NMR $(CDCl_3)$ δ 8.20 (s, 1 H, CH=), 4.92 (t, J= 2 Hz, 2 H, Cp), 4.71 (t, J= 2 Hz, 2 H, Cp), 4.33 (dd, J= 5.1 Hz, 2 H, CH_2O_2C), 4.18 (s, 2 H, $CpCH_2O$), 4.17 (s, 4 H, Cp), 3.60 (m, 2 H, OCH_2), 1.82 (m, 2 H, CH_2), 1.65 (m, 6 H, CH_2's); ^{13}C NMR $(CDCl_3)$ δ 163.3 (CO_2), 158.2 $(CH=)$, 116.9 (CN), 97.8 $(=C(CN))$, 88.6 (ipso-Cp), 75.0 $(CpOCH_2)$, 73.9 (Cp CH), 72.7 (Cp CH), 71.7 (CH_2O_2C), 70.1 (Cp CH), 68.8 (Cp CH), 68.3 (CH_2O), 29.8, 28.0, 26.6, 26.4 $(CH_2$'s). Anal. Calcd for $C_{21}H_{23}NO_3$: C, 64.14; H, 5.89%. Found: C, 63.64; H, 6.00%.

Lactone 10b Lactone 10b was purified by column chromatography (2 x 15 cm) on alumina. Elution with $MeOH/CH_2Cl_2$ (1/9, v/v) gave a dark purple band which was collected and the solvents removed to afford pure lactone as a purple solid. ^1H NMR $(CDCl_3)$ δ 8.25 (s, 1 H, CH=), 5.11 (t, J= 2 Hz, 2 H, Cp), 5.04 (s, 2 H, CH_2), 4.79 (t, J= 2 Hz, 2 H, Cp), 4.57 (t, J= 2 Hz, 2 H, Cp), 4.20 (t, J= 2 Hz, 2 H, Cp); ^{13}C NMR $(CDCl_3)$ δ 158.9 (CO_2), 74.1 (Cp CH), 72.8 (Cp CH), 69.1 (CH), 68.0 (CH), 63.7 (CH_2O).

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Captions for Figures

Figure 1. Drawings for the single-crystal molecular-structures of complexes **1a-d**. Thermal ellipses for non-hydrogen atoms are drawn to encompass 30% of the electron density and hydrogen atoms are depicted with arbitrarily small thermal spheres for clarity.

Figure 2. Drawing for the single-crystal molecular-structure of lactone **10a**. Thermal ellipses for non-hydrogen atoms are drawn to encompass 30% of the electron density and hydrogen atoms are depicted with arbitrarily small thermal spheres for clarity.
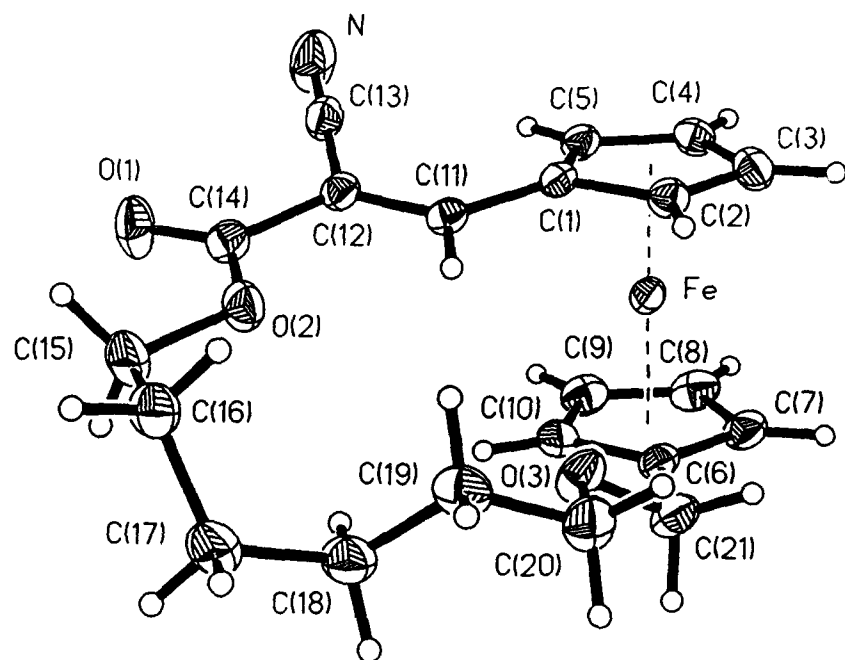
Figure 1

1a

1b

1c

1d
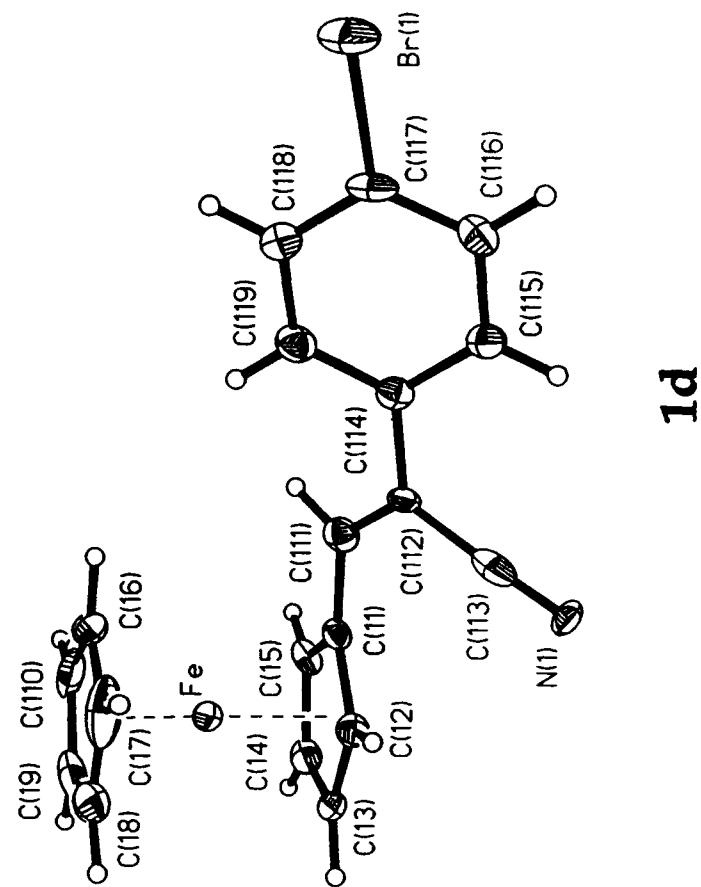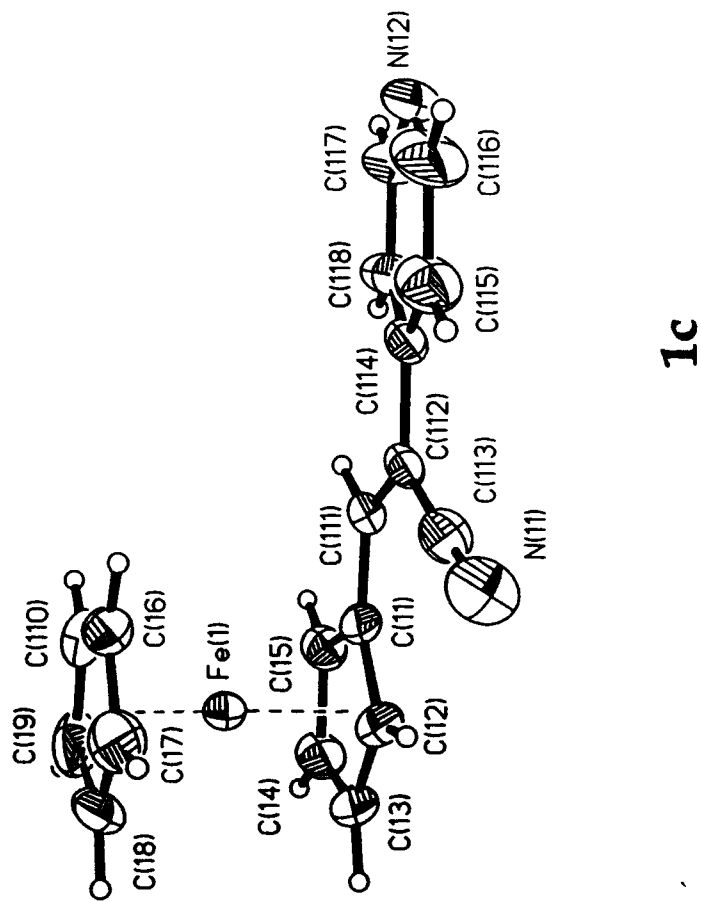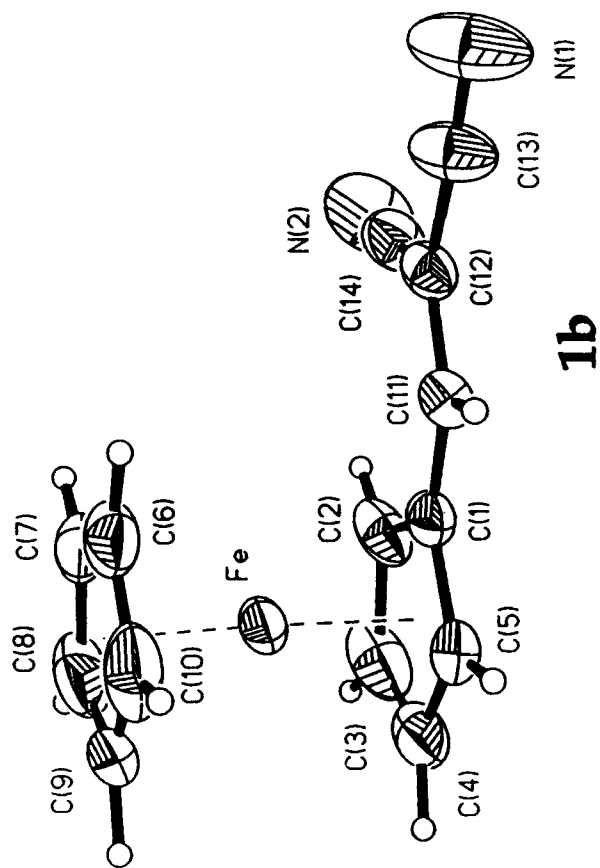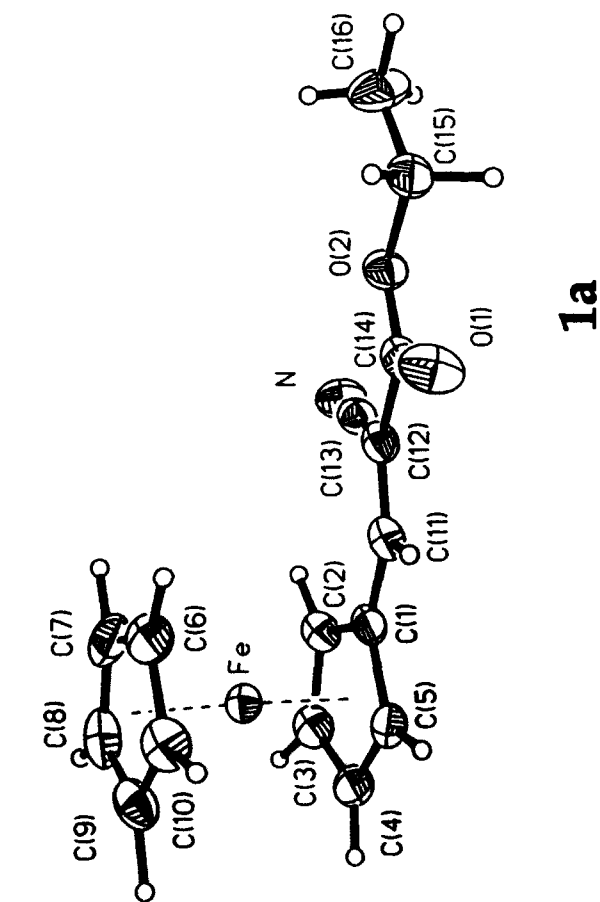
Figure 2

Table 1. Summary of Pertinent Crystallographic Data for the Single-Crystal Molecular-Structure Studies of Complexes 1a-d.

		Complex		
	1a	1b	1c	1d
formula	$C_{15}H_{15}FeNO_2$	$C_{14}H_{10}FeN_2$	$C_{18}H_{14}FeN_2$	$C_{19}H_{14}BrFeN$
fw	309.1	262.1	314.2	392.1
Unit Cell	$a = 12.667\ (4)$ Å	$a = 6.207\ (1)$ Å	$a = 13.353\ (2)$ Å	$a = 11.226\ (2)$ Å
	$b = 7.555\ (1)$ Å	$b = 19.054\ (5)$ Å	$b = 10.705\ (2)$ Å	$b = 10.477\ (3)$ Å
	$c = 15.137\ (4)$ Å	$c = 10.599\ (4)$ Å	$c = 15.837\ (3)$ Å	$c = 27.368\ (5)$ Å
	$\alpha = 90.0°$	$\alpha = 90.0°$	$\alpha = 86.2\ (1)°$	$\alpha = 90.0°$
	$\beta = 98.85\ (2)°$	$\beta = 103.4\ (2)°$	$\beta = 76.2\ (1)°$	$\beta = 101.5\ (1)°$
	$\gamma = 90.0°$	$\gamma = 90.0°$	$\gamma = 82.6\ (1)°$	$\gamma = 90.0°$
	$V = 1431.7\ (6)$ Å^3	$V = 1219.4\ (6)$ Å^3	$V = 2177.9\ (6)$ Å^3	$V = 3153.8\ (12)$ Å^3
	$Z = 4$	$Z = 4$	$Z = 6$	$Z = 8$
Space Group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
D_{calc}, g/cm^3	1.434	1.428	1.437	1.651
μ (Mo_α), mm^{-1}	1.05	1.21	1.03	3.46
Scan Type	2θ-θ	2θ-θ	2θ-θ	2θ-θ
Scan Speed, deg/min	Var.; 3.0 to 14.65	Var.; 3.0 to 14.65	Var.; 3.0 to 14.65	Var.; 3.0 to 14.65
Scan Range, 2θ in deg	3.0 to 50.0	3.0 to 50.0	3.0 to 50.0	3.0 to 50.0
Total Data	2841	2487	8350	6952
Unique Data	2624	2153	7722	5590
Data with $(F_o) > (n)\sigma(F)$	1999	1394	5780	3759
# of parameters refined	182	154	569	397
R	3.44%	6.03%	4.64%	5.86%
R_w	4.14%	7.09%	8.82%	6.17%
GOF	1.30	1.15	0.60	1.18